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CITATION:

Ono, Sozaburo. The photographic action of sputtered platinum films. The Review of Physical Chemistry of Japan 1937, 11(2): 76-81

ISSUE DATE:

1937-09-15

URL:

http://hdl.handle.net/2433/46506

THE PHOTOGRAPHIC ACTION OF SPUTTERED PLATINUM FILMS.

By Sôzaburo Ono.

Many studies[1] have been made on the photographic action of various metal surfaces since the discovery of this effect by Russel,[2] but as yet there is no satisfactory theory to explain this phenomenon. Among the various theories introduced the theory of " Hydrogen-peroxide Formation " first proposed by Russel and supported by many other investigators seems to be most inviting. Aoyama and Fukuroi[3] have concluded that the photogrpahic action of a polished metal surface was caused by the gas activated at the surface and desorbed from it. The gas immediately acted on a photographic plate and produced a latent image thereon. If the photographic action is caused by the interaction between the metal and the gas in contact with it, and is correlated to the activation and desorption of the gas, it is quite probable that some relationship between the catalytic activity and the photographic action may be found. The present research is undertaken to see whether this relationship exists or not. Though the results obtained is not conclusive, some characteristics of the photographic action of the platinum films have been observed.

Experimental.

The platinum films were made by means of cathode sputtering, employing first a sputtering vessel[4] similar to that used by Finch and others, and afterwards using the one[5] shown in Fig. 1.

K is a cathode made of platinum plate, 4 cm. in diameter and 0.3 mm. thick; A is an anode made of aluminium plate, 4 cm. in diameter. A glass support, C, is put on A; and on C is placed B, a 2 cm. square glass plate, on whose surface a film is made. The distance from K to A is 2.5 cm., and that from K to B 0.9 cm.

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1) G. L. Keenan, *Chem. Rev.*, 3, 95 (1926).

2) W. J. Russel, *Proc. Roy. Soc.*, 61, 424 (1897); 63, 102 (1898).

3) S. Aoyama, T. Fukuroi, and I. Takahashi, *Bull. Inst. Phys. Chem. Res.*, 12, 493 (1933);
S. Aoyama and T. Fukuroi, *ibid.*, 14, 481 (1935);
S. Aoyama, T. Fukuroi, and N. Suzuki, *ibid.*, 15, 923 (1936).

4) This vessel (V_1) is convenient for preparing two films having the same degree of activity simultaneously: G. I. Finch, C. A. Murison, N. Stuart and G. P. Thomson, *Proc. Roy. Soc.* (A), 141, 423 (1933).

5) This vessel (V_2) is convenient for preparing a film with homogeneous activity over the whole surface.

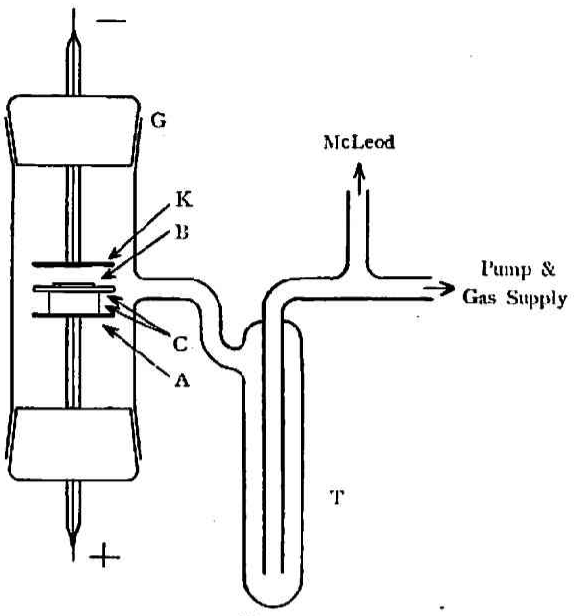

Fig. 1.

A direct current of high voltage was used. The alternating current was stepped up, rectified, and smoothed by means of a transformer, the Kenotron and a 2 μ F. condenser, respectively. Oxygen was preferably used instead of hydrogen for the filling gas, because when the catalytic activities were compared by the rate of the oxy-hydrogen reaction, a catalyst produced in hydrogen, as many investigators[6] have pointed out, proved to be far more inactive than that produced in oxygen. Commercial oxygen which was purified with platinum asbestos, scale-like caustic potash, and phosphorus pentoxide was used.

To prevent the catalytic activity from decreasing, the mercury and organic vapours in the system were removed as much as possible, by cooling Trap T in Fig. 1 with solid carbon dioxide, and making a ground-glass-joint G in Fig. 1 vacuum tight with gas-free bee wax.

Many films possessing various degrees of activity could be made in the range from 0.15 to 0.5 mm. Hg in the pressure, from 500 to 1500 volts in the potential, and from 20 to 40 m. A. in the current, respectively. While on the one hand, one[7] of the most active films of 3 square cm. was able to catalyze the oxy-hydrogen reaction such that the pressure of the mixture in a vessel of 200 c.c. decreased from 30 to 3 cm. Hg in one minute and a half, and the film became red due to the heat produced in the reaction; on the other hand, one of the most inactive films could not catalyze the reaction under the same conditions at all. As to the relations between the activities and other properties of films and conditions of sputtering, similar behaviours to those in the case of Finch and others were observed.

The author examined the difference between a film catalyst and a polished platinum plate with respect to the photographic action. By using hydrogen and oxygen[8] as the filling gas, a number of experiments were carried out at room

6) 4). and G. Bredig u. R. Allolio, *Z. phys. Chem.* [A], **126**, 41 (1927) & etc.

7) The conditions under which the catalyst was prepared were as follows: the pressure of oxygen was 0.4 mm. Hg; the current density was 3.2 m. A./cm^2.; the potential was 650 Volts; the duration of time was 20 minutes.

8) When oxygen was used, the catalyst was at first activated with hydrogen, and after evacuating, filled with oxygen.

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temperatures in the range from 0.5 to 20 cm. Hg in the pressure, from one to five days in the duration of time, from 0.5 to 1.5 mm. in the distance between a film and a plate, respectively. The photographic action of a film catalyst was compared with that of a polished platinum plate under the same conditions. The latter gave the photographic action similar to that in the case of Aoyama, while the former had no effect on any of the photographic plates, such as Oriental Process Plate, Illford Special Rapid Plate, Illford Highpersensitive Panchromatic Plate and Oriental Infra-red Plate. Therefore, it seems obvious that the film catalyst is quite different from the polished surface so far as the photographic action is concerned.

As described above, the photographic action was never caused by the film catalyst in oxygen or hydrogen alone. On the other hand, in the oxy-hydrogen reaction[9] the film catalyst brought forth the action, which is given in Fig. 2.[10]

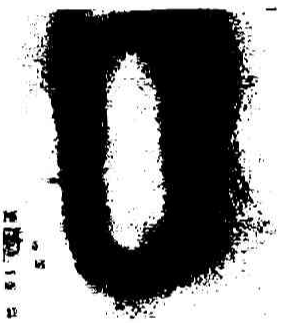

Fig. 2.

As has been mentioned already, a sudden reaction in the presence of a highly active catalyst caused a red heating of the film which made the photographic action on even infra-red plates. When the reaction amount was decreased and the temperature of the film was relatively low, neither infra-red nor panchromatic plates were affected, but the pre-exposed Oriental Process Plate and Illford Special Rapid Plate were affected. Accordingly, the order of the sensitivities of the plates used for the catalysts possessing the same degree of activity was as follows: (1) Oriental Process Plate, (2) Illford Special Rapid Plate, (3) Fuji Infra-red Plate, and (4) Illford Hypersensitive Panchromatic Plate.

The influence of the temperature of the catalyst on the photographic action was examined under the following conditions. To one of the two films having the same degree of activity a rapid stream of a fixed quantity of hydrogen and oxygen was introduced and to the other the same quantity of the mixture at about a tenth of the rate as in the former, and then both were left in contact with the gases for the same duration of time. The faster the stream of the gases

9) The ratio of hydrogen to oxygen was stoichiometrical.

10) The catalyst prepared in the vessel V_1 (see note 4) was used, and it was parabollic and about 5 square cm. The conditions under which this photograph was taken at room temperatures were as follows; the plate was an Oriental Process Plate; the distance between the plate and the catalyst was 1.5 mm.; the amount of the reacting gas was 50 c.c. under N. T. P. As it is seen in Fig. 2, an image appears on the part of the plate facing the edges of the catalyst.

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introduced, the faster the reaction and the higher is the temperature of the catalyst. The photographic action of the former was stronger than that of the latter. And it is admitted from the experiments that the photographic action is qualitatively proportional to catalytic activity. Thus the author could obtain some qualitative results on the specific nature of the photographic action in the oxy-hydrogen reaction and the sensitivities of plates.

Which, then, causes this photographic action: radiation or active particles? If the former causes the action, what wave length will it be? Again, if the latter causes it, can it be determined chemically? If the active particles bring forth the action, the latent image should "deviate" towards the direction of flow when a reacting gas is passed over the catalyst with an adequate velocity. This effect was investigated with a set-up represented schematically in Fig. 3A,

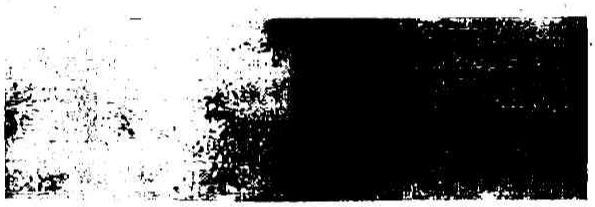

Fig. 3.

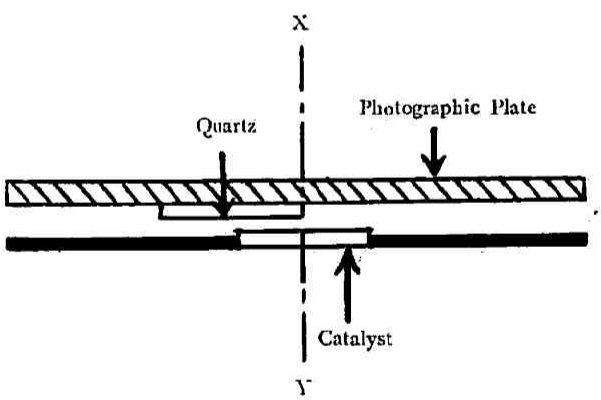

Fig. 3A.

in which a catalyst,[11] 2 cm. square, was placed in such a manner that X–Y axis bisected it and at the same time this axis was colinear with the right hand side edge of a quartz plate, 2 cm. square and 0.4 mm. thick, fixed on the Illford Special Rapid Plate, which was set one mm away from the catalyst; and using a rapid stream flowing from left to right of an oxy-hydrogen gas mixture produced by the expansion into vacuum. As it is seen in Fig. 3, there is no image on the left half of the plate, where it is covered with or without the quartz plate.

11) This catalyst was prepared in the vessel V_2 (see note 5).

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An image, however, appears on the right half although it does not "deviate" markedly[12]; there is, nevertheless, some fogging or a faint tail visible. This evidence indicates that the photographic action in the oxy-hydrogen reaction is not due to radiation which is able to penetrate a quartz plate, and this justifies the assumption that the action is brought forth by the active particles produced.

The following experiments were carried out to make a further confirmation of it by means of chemical methods. The results obtained indicated that the latent image was produced mainly by hydrogen peroxide. It was determined by the oxidation of KI in a KI-starch film. By adding potassium iodide to a 5% solution of soluble starch, $\frac{1}{100}$ N potassium iodide starch solution was prepared, which was dried on a glass plate. The film thus prepared was semi-transparent, and whitish in colour. When this film was used instead of a photographic plate, red iodine was observed on the film. When water was poured on it after the reaction, it turned blue, which indicated the iodine-starch reaction. The substance which made the photographic action, therefore, was most probably either hydrogen peroxide or ozone. In addition, the action on potassium permanganate was studied in order to differentiate between hydrogen peroxide and ozone. Kaolin kneaded with water was coated on a glass plate and dried; it was then soaked in a potassium permanganate solution to make a film, which was brownish pink-tinted. When this film was used, it was decolorized. Further, the different photographic plates were sealed in the hydrogen peroxide vapour mixed with that of water, and the sensitivities of these were compared. The results were in good agreement with the order of the sensitivities of the photographic plates to the same photographic action caused by the catalyst. From these evidences, it may be concluded that the photographic action was brought forth mainly by hydrogen peroxide and not by ozone.

Polyakow[13] has found in the oxy-hydrogen reaction in the presence of a platinum wire heated to 400°—450°C. that, in addition to the surface reaction caused by the catalyst, the active substances released from the surface of the catalyst brought forth the chain reaction in the gaseous phase, and that hydrogen peroxide and very small quantity of ozone which were the reaction products condensed on the walls. Kobosew[14] has also found in a similar reaction in the presence of "platin mohr" at room temperatures that the reaction proceeded similarly, and that atomic hydrogen and hydrogen peroxide were formed in the gaseous phase.

In the present experiments it was found that the photographic action was brought forth

12) It seems probable that with a higher velocity the "deviation" should be more marked.

13) M. W. Polyakow and Others, *Acta Physicochim. U. R. S. S.* 1, 817 and 821; 2, 397 (1935).

14) K. I. Kobosew and W. L. Anochin, *Z. phys. Chem.* [B], 13, 63 (1931).

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mainly by hydrogen peroxide.[15] Taking the above two cases into consideration, however, it can not be denied that atomic hydrogen as in the latter case and ozone as in the former case may take part in the photographic action.

Summary and Conclusion.

The platinum film catalysts have been prepared by means of cathode sputtering in oxygen.

The difference between the surface of a polished platinum and that of a sputtered platinum film catalyst is obvious from the circumstance that the latter does not cause the photographic action in hydrogen or oxygen alone, while the former does manifest this action.

When a platinum film catalyzes the oxy-hydrogen reaction, it seems certain that hydrogen peroxide or something which is easily changeable to hydrogen peroxide is present in the gaseous phase, and the photographic action is mainly due to it.

Whether the difference between the photographic action of a polished metal surface and that of a film catalyst is fundamental or not will be discussed in a further research.

The author wishes to express his most sincere appreciation to Prof. S. Horiba for his guidance throughout this research.

This is the paper presented to Committee of Catalysis of Japan Society for the Promotion of Scientific Research.

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(Received June 8, 1937.)

15) There is no experimental foundation for the assumption that it is not due to the evaporation of hydrogen peroxide from the surface of the catalyst.